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13. SUPPLEMENTARY NOTES

14. ABSTRACT   Low-temperature growth of indium nitride (InN) films on gallium nitride(0001) substrates was achieved by supersonic jet epitaxy using ammonia (NH_3) and trimethyl-indium (TMIn). Unfortunately, there was no indication of a reaction pathway involving TMIn and NH_3 that results in InN growth at temperatures less than approximately 500°C. We infer that NH_3 decomposition is the rate-limiting step in InN growth using NH_3 and elemental In or TMIn. Highly selective generation of ground-state nitrogen atoms for growth was accomplished using a radio-frequency (rf) discharge supersonic jet source. The rf discharge supersonic jet source was characterized by optical emission spectroscopy and time-of-flight appearance potential mass spectrometry.

15. SUBJECT TERMS

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Title: CHEMICAL BEAM EPITAXY OF INDIUM NITRIDE USING SEEDED SUPERSONIC BEAMS OF AMMONIA AND TRIMETHYL-INDIUM

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Introduction

The III-nitride semiconductors (AlN, GaN and InN) continue to be the focus of intensive research and development activity due to their applications in blue light-emitting devices and high-temperature, high-frequency microelectronic devices [1]. Most of the recent emphasis has been on the development of GaN (E_g = 3.45 eV) materials for blue light-emitting diodes (LEDs) and laser diodes [2]. Successful development of InN (E_g = 1.9 eV) materials will allow fabrication of orange and red light-emitting devices, an important step in the evolution of nitride-based optoelectronics. Moreover, InN is a candidate for use in microelectronic devices, such as high electron mobility transistors (HEMTs). InN films have been grown by a variety of methods including rf sputtering [3], plasma-assisted metal-organic vapor phase epitaxy (plasma-MOVPE) [4], plasma-assisted molecular beam epitaxy (plasma-MBE) [5], atomic layer epitaxy (ALE) [6], and, more recently, MOVPE using ammonia (NH_3) [7]. The typical substrate has been sapphire, despite the poor lattice match; however, InN films with superior electrical properties have been grown recently on MOVPE GaN substrates [8]. The indium sources used in these studies include elemental In, trimethyl-indium (TMIn), triethyl-indium (TEIn), and ethyldimethyl-indium (EDMIn). NH_3 and plasma-excited molecular nitrogen have been used as nitrogen sources. Progress in the epitaxial growth of InN films for device applications has been hindered

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by the low thermal stability of InN. The equilibrium N_2 pressure over InN is much higher that over AlN and GaN [9], and this restricts typical epitaxial growth temperatures to less than 500°C.

Growth temperatures less than 500°C limit the nitrogen incorporation efficiency of NH_3 and necessitate the use of very large V/III flux ratios in InN MOVPE. A very low reaction efficiency is also observed for NH_3 nitridation of elemental Ga temperatures at less than 500°C [10]; however, NH_3 is known to undergo dissociative chemisorption on the GaN(0001) Ga-polar surface at room temperature to produce adsorbed NH_x and H moieties [11, 12]. Temperature-programmed desorption experiments on GaN films indicate that most of the adsorbed NH_3 desorbs by recombination of NH_x and H at approximately 300°C [12]. A small amount of irreversible chemisorption (e.g., nitridation) occurs, as evidenced by a H_2 desorption peak at a slightly higher temperature. A previous study on polycrystalline GaN films indicated that H_2 desorption from N sites (e.g., NH_x moieties) required higher temperatures (~500°C) than H_2 desorption from Ga sites (~250°C) [13]. These observations suggest that H_2 desorption from NH_x moieties limits the nitridation efficiency of NH_3 at low temperatures. A similar situation is expected for NH_3 nitridation of elemental In. There is some ambiguity in the literature regarding the crystalline quality of InN films deposited at low temperatures. Bedair and coworkers [6] reported that a very narrow temperature window near 480°C exists for ALE growth of monocrystalline InN films on sapphire using EDMIn and NH_3. Films grown at lower temperatures were polycrystalline, and the ALE growth rate was suppressed markedly by InN decomposition at higher substrate temperatures. In contrast, InN films with the best reported crystalline quality, as measured by a 96-arcsec FWHM of the InN(0001) x-ray rocking curve, were grown on sapphire by MOVPE at 375°C using TMI and NH_3 [7]. Unfortunately, electrical characterization data were not reported for these films; however, InN films grown by MOVPE at 450°C on GaN substrates had a Hall mobility of approximately 700 $cm^2s^{-1}V^{-1}$ at an electron concentration of 5×10^{19} cm^{-3} [8].

Research Issues

- High *n*-type conductivity of InN films due to nitrogen vacancies and/or electrically active impurities.

- Low nitrogen incorporation efficiency of NH_3 at substrate temperatures typically employed for InN growth.
- Poor crystalline quality of InN films deposited at low temperatures due to restricted surface adatom mobility.

Suppositions

- Low reaction efficiency of NH_3 with elemental Ga (and by extension In) at temperatures less than 500°C is due to slow H_2 desorption kinetics.
- Hydrogen transfer between adsorbed In alkyl and NH_x moieties may provide a reaction pathway for low-temperature InN growth.
- Hyperthermal kinetic energy of In precursor can be used to improve crystalline quality of InN films grown at low temperatures by enhancing surface adatom mobility.

Approach

This research project explored low-temperature growth of InN films by supersonic jet epitaxy (SJE), a novel chemical beam epitaxy (CBE) technique that employs intense, monoenergetic beams of precursor molecules [14]. The supersonic molecular beams used for growth are generated by expanding a gas mixture through a small orifice into vacuum. The precursor fluxes achievable with supersonic molecular beams are higher than can be obtained using conventional effusive sources. By seeding the growth precursors in a light carrier gas (e.g., He or H_2) beams of precursor molecules with hyperthermal velocities and narrow (non-Boltzmann) kinetic energy distributions are obtained. Heavier precursor molecules seeded in He supersonic beams attain kinetic energies of 0.2 eV to greater than 5 eV, depending on their molecular weight and the pre-expansion (stagnation) temperature. The directed kinetic energy of molecules in seeded supersonic beams can be used to overcome activation barriers to (i) precursor decomposition and (ii) adatom surface migration, resulting in higher incorporation efficiencies and better crystalline quality in epitaxial growth.
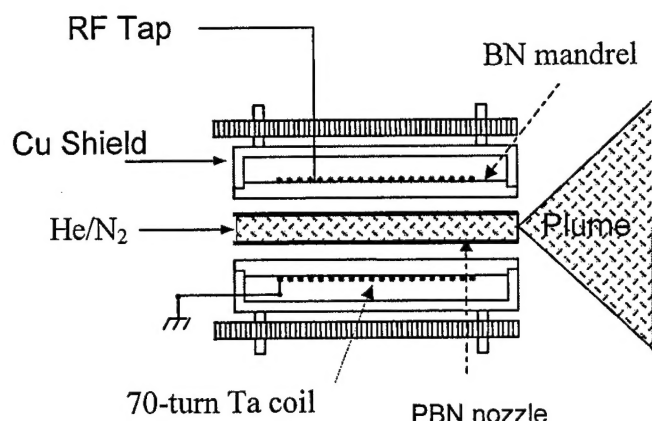
The remarkable intensities achievable with seeded supersonic beams are illustrated by the peak growth rate of 0.25 μm *per second* obtained by Eres, *et al.* for the heteroepitaxial growth of Ge using a supersonic free jet of 5% digermane in He [15]. Mullins and coworkers [16] demonstrated that imparting hyperthermal kinetic energy to disilane by seeding in H_2 increases

its reaction probability in Si homoepitaxial growth. Ho and coworkers [17] have demonstrated that the growth temperature of β-SiC on Si(111) can be lowered to 560°C by using methylsilane seeded in He or H_2. Moreover, the growth rate and crystalline quality of the epitaxial SiC films are enhanced. We employed hyperthermal TEGa beams and NH_3 from a UHV leak valve to grow homoepitaxial GaN films on MOVPE GaN(0001) substrates at 700-750°C [18]. The surface morphology of these films was superior to homoepitaxial GaN films grown by gas-source MBE using NH_3 and elemental Ga. These achievements provided a scientific rationale for developing a low-temperature InN SJE process using TMIn and NH_3 as precursors.

Experiment

The SJE experiments were performed using a custom-built apparatus equipped with dual supersonic jet sources, a UHV leak value for back-filling the growth chamber with NH_3, and a Knudsen cell for elemental In [19]. The SJE chamber is equipped with reflection high-energy electron diffraction (RHEED), desorption mass spectroscopy (DMS) [20], and optical reflectivity tools for in situ growth monitoring. Two quadrupole mass spectrometers (QMS) are available: a UTI-100C interfaced to LabView for DMS and a cross-beam Hiden HAL-301 triple mass filter mounted on a rotatable table for time-of-flight (TOF) measurements of the seeded supersonic beams. X-ray photoelectron spectroscopy (XPS) is available on-line in an adjacent surface analysis chamber. The surface analysis chamber is equipped with a PHI 3057 XPS system comprising a 10-360 spherical capacitor analyzer (SCA), Omni Focus III fixed-aperture lens, 16-element multichannel detector, and 257 DR11 PC interface card. A 400 W dual Al/Mg anode x-ray source is used.

TMIn was supplied from a commercial stainless steel bubbler (Epichem "Solution Trimethyl-indium"). Anhydrous NH_3 (electronics grade) was supplied by Air Products and further purified by passage through a Nanochem unit (Matheson). The substrates were 1.5-2 μm thick GaN(0001) films grown by MOCVD on on-axis 6H-SiC using a 0.1-μm AlN buffer layer. The substrates are coated on the backside (SiC face) with tungsten and cut into $1 \times 1 \ cm^2$ pieces. *Ex situ* cleaning was effected by ultrasonic degreasing in trichloroethylene for 20 min. The substrates were initially atomically smooth with a roughness of 0.17 nm RMS, as determined from $1 \times 1 \ \mu m^2$ atomic force microscopy (AFM) images. *In situ* cleaning at 800°C by annealing in an NH_3 ambient (1.5×10^{-5} Torr) removed oxygen and carbon contamination from the surface.
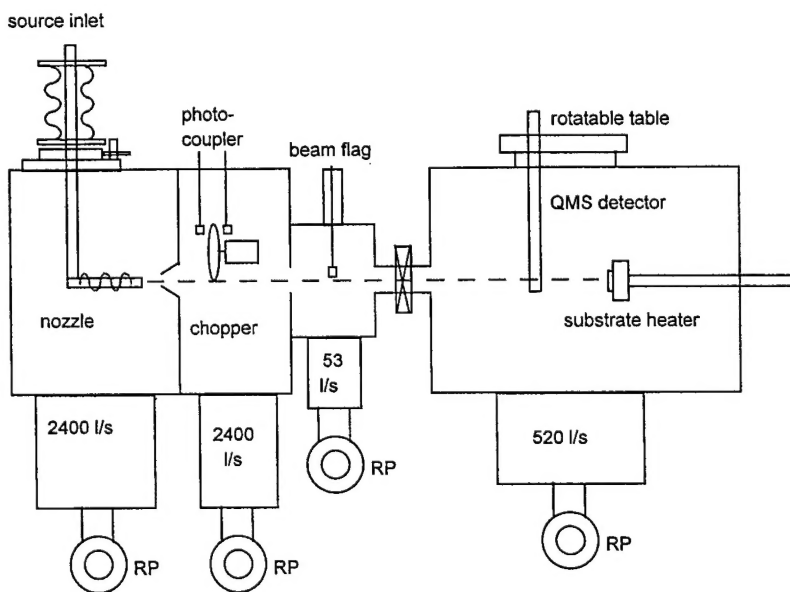
Fig. 1. Schematic of rf-discharge supersonic jet N atom source.

The resultant growth surface exhibited a $\sqrt{3} \times \sqrt{3}$ R30° reconstruction but was rougher (0.28 nm RMS) than the surface before cleaning [21].

A supersonic jet N atom source was constructed using the rf coaxial resonator design (Fig. 1) originally published by Pollard [22]. The resonator consists of a multi-turn helical coil wrapped around a BN mandrel to which ~100 W 13.56 MHz rf power is applied. The rf frequency is apparently not critical, as Pollard used 38 MHz rf and Sellidj, *et al.* later employed 13.56 MHz rf power with a similar resonator design [23]. The N_2/He plasma is contained within an inner coaxial pyrolytic BN (PBN) tube with a laser-drilled 150-μm orifice. Nozzle stagnation pressures of ~100 Torr are typically achieved during stable operation. Time-of-flight appearance potential mass spectrometry (TOF-APMS) experiments were performed using the supersonic molecular beam scattering apparatus shown in Fig. 1. The rf discharge supersonic free jet was skimmed and collimated using three stages of differential pumping. The detection system, including the rotating beam chopper, triple-filter QMS and multi-channel scalar card, serves two purposes i) it provides excellent separation of the beam and background QMS signals and ii) provides TOF velocity data on species in the terminal beam. OES measurements of the plasma

Fig. 2. Schematic of supersonic molecular beam scattering apparatus.

plume are facilitated by a sapphire viewport located directly above the skimmer.

Results and Discussion

InN growth experiments were performed using elemental In from a Knudsen cell and a seeded supersonic beam of 10% NH_3 in H_2. MOVPE-grown GaN(0001) on AlN-buffered 6H-SiC substrates were used to provide a chemically compatible surface for InN nucleation. InN growth was attempted at substrate temperatures of 480-600°C. The NH_3 flux at the substrate position was approximately 5×10^{15} cm^{-2} s^{-1}, and the In flux was varied from 7.5×10^{11} to 1.9×10^{14} cm^{-2} s^{-1} to provide V/III flux ratios ranging from 26 to 6,670 (Table 1). The average kinetic energy of NH_3 molecules in these experiments was estimated to be 0.3 eV, assuming an ideal supersonic expansion with zero velocity slip. The InN growth rates were very low for all experimental conditions. Metallic In accumulation was detected by XPS if the incident In flux exceeded the theoretical In desorption flux at the substrate temperature, *i.e.*, the substrate temperature was less than the In condensation temperature. InN growth was suppressed at substrate temperatures greater than 500°C due to thermal decomposition. An SEM image of an InN film grown at 480°C using an In flux of 7.5×10^{11} cm^{-2} s^{-1} is shown in Fig. 3. The InN film was patchy with a maximum thickness of 100 nm after 30 h of growth. The rough surface morphology is suggestive of Volmer-Weber growth.

Table 1. Experimental conditions for InN growth on GaN(0001) using NH_3 seeded in H_2

Substrate temp.	In K-cell temp.	NH_3 flow rate	NH_3 flux	In flux	In cond. temp.	Growth time
(°C)	(°C)	(sccm)	$(cm^{-2}s^{-1})$	$(cm^{-2}s^{-1})$	(°C)	(hr)
480	757	30	5.0E+15	4.0E+13	573	5
555	757	30	5.0E+15	4.0E+13	573	2
600	757	30	5.0E+15	4.0E+13	573	3.3
480	605	30	5.0E+15	7.5E+11	469	30

Heteroepitaxial growth of InN on MOCVD-grown GaN(0001) substrates was attempted using seeded supersonic molecular beams of TMIn in He and NH_3 background pressures of 1.0×10^{-5} to 1.0×10^{-4} Torr. The average kinetic energy of TMIn molecules in these experiments was estimated to be ~2 eV, assuming an ideal supersonic expansion with zero velocity slip. The maximum NH_3 pressure was limited by the need to maintain molecular flow conditions within SJE growth chamber. The substrate temperature (320-520°C) and TMIn flow rate (0.06 – 0.37 sccm) were varied to provide a wide range of potential growth conditions, as summarized in

Table 2. The nominal V/III flux ratios in these experiments ranged from 80 to 5300. The In condensation temperature was calculated from the In flux by assuming a sticking coefficient of unity for TMIn. The condensation temperature represents the minimum substrate temperature
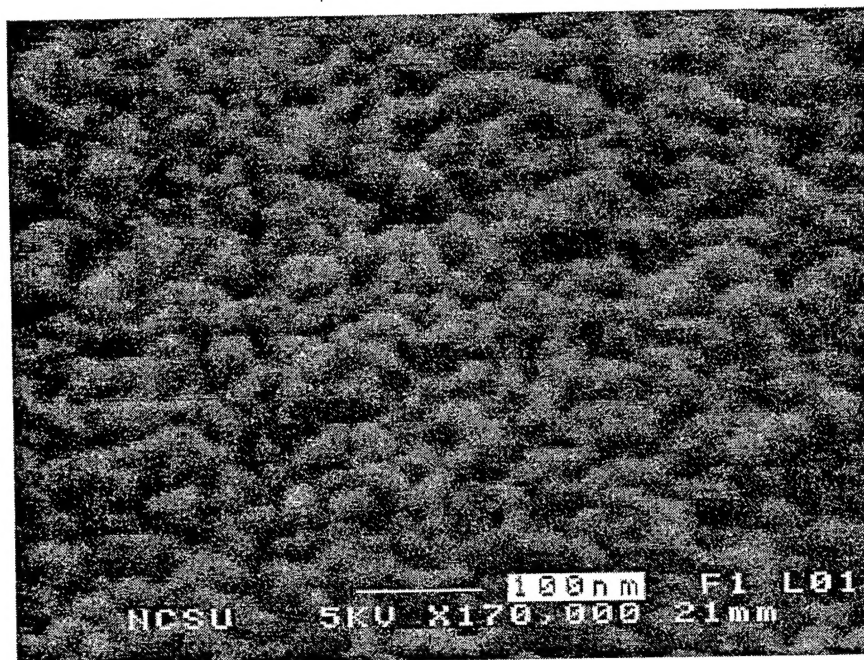

Fig. 3. Top-view SEM image of an InN film on GaN grown at 480°C using an In flux of 7.5×10^{11} cm^{-2} s^{-1} and an NH$_3$ flux of approximately 5×10^{15} cm^{-2} s^{-1}.

required to prevent accumulation of metallic In on the substrate in the *absence* of reaction with NH$_3$ to form InN.

XP spectra and SEM images indicated the deposition of metallic In under the chosen growth conditions. The amount of deposited In was limited at the lower substrate temperatures (<400°C) by the decomposition rate of TMIn. XPS evidenced the amount of In on the substrate increased in direct proportion to the incident TMIn flux for substrate temperatures greater than 400°C. SEM images of films grown under the most promising conditions (Fig. 4) revealed the presence of spherical In droplets on the substrate after the growth experiments. Energy-dispersive x-ray (EDX) analysis (resolution: 0.5 μm) verified that the droplets contained In. The surface regions between the droplets in Fig. 4a have a roughened appearance similar to that of the InN film shown in Fig. 3, and growth pits are evident between the droplets in Fig. 4b. We infer from these observations and the close similarity of the growth temperatures to that required

to achieve InN growth on GaN(0001) using elemental In and NH₃ (*vide supra*) that the substrates are covered by very thin InN layers. We estimate that the InN growth rates under these conditions are extremely low (less than 3 nm/h).

Table 2. Experimental conditions for InN growth on GaN(0001) using TMIn seeded in He.

Substrate temp.	TMIn flow rate	NH₃ pressure	NH₃ flux	TMIn flux	In cond. temp.	Growth time
(°C)	(sccm)	(torr)	$(cm^{-2}s^{-1})$	$(cm^{-2}s^{-1})$	(°C)	(hr)
320	0.24	1.00E-05	4.9E+15	3.9E+13	570	4
380	0.37	1.00E-05	4.9E+15	6.1E+13	581	4
380	0.24	1.00E-05	4.9E+15	4.0E+13	570	4
480	0.22	1.00E-05	4.9E+15	3.7E+13	570	4
480	0.06	1.00E-05	4.9E+15	9.4E+12	530	4
520	0.24	1.00E-05	4.9E+15	4.0E+13	570	4
500	0.24	1.00E-05	4.9E+15	4.0E+13	570	4
500	0.24	1.00E-04	4.9E+16	4.0E+13	570	4
480	0.24	1.00E-04	4.9E+16	4.0E+13	570	4
520	0.06	1.00E-04	4.9E+16	9.3E+12	530	8
500	0.12	1.00E-04	4.9E+16	2.0E+13	552	8
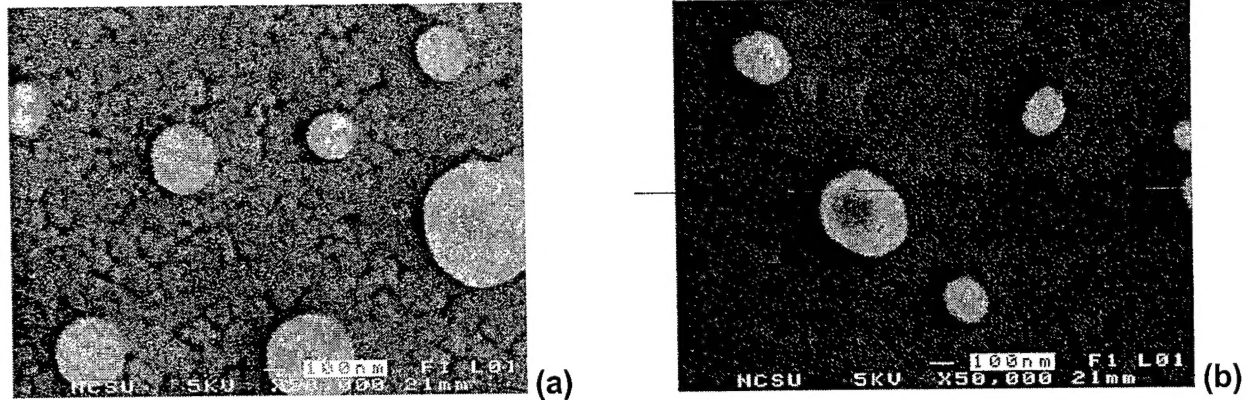
Fig. 4. Top-view SEM images of InN films grown on GaN(0001) using a TMIn flux of 4.0×10^{13} cm^{-2} s^{-1} and an NH₃ flux of 4.9×10^{16} cm^{-2} s^{-1} at substrate temperatures of (a) 500 and (b) 480°C.

Indium accumulation can be avoided by reducing the TMIn flux and/or increasing the substrate temperature, but either choice will result in unrealistically low growth rates. Unfortunately, there is no evidence of a reaction pathway involving TMIn and NH₃ that results in InN growth at temperatures less than approximately 500°C. We infer that NH₃ decomposition is the rate-limiting step in InN growth using NH₃ and elemental In or TMIn.

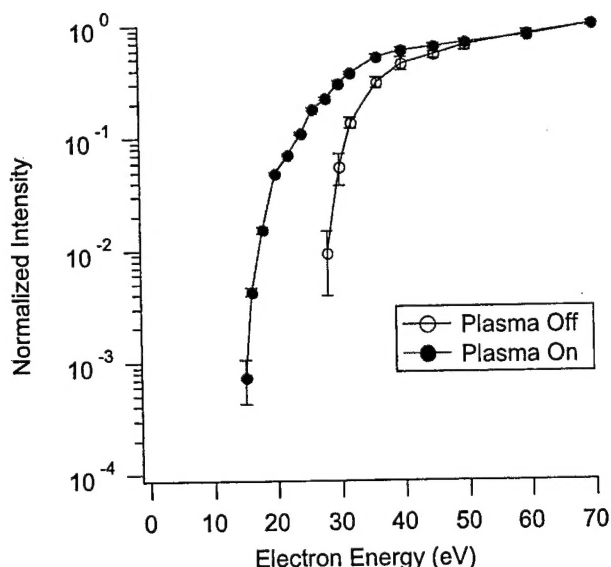**Fig. 5. TOF-APMS (14 amu) data characterizing an 13.56 MHz rf discharge N atom source.**

Highly selective generation of ground-state N atoms for future III-nitride film growth experiments was accomplished using an rf discharge supersonic jet source (Fig. 1). In the design originally published by Pollard, a flowing He/N_2 mixture is subjected to rf excitation at a moderately high pressure (~100 Torr) inside a tube (nozzle) fabricated from BN [22]. The resultant plasma expands through an orifice into vacuum forming a supersonic free jet "plume" that c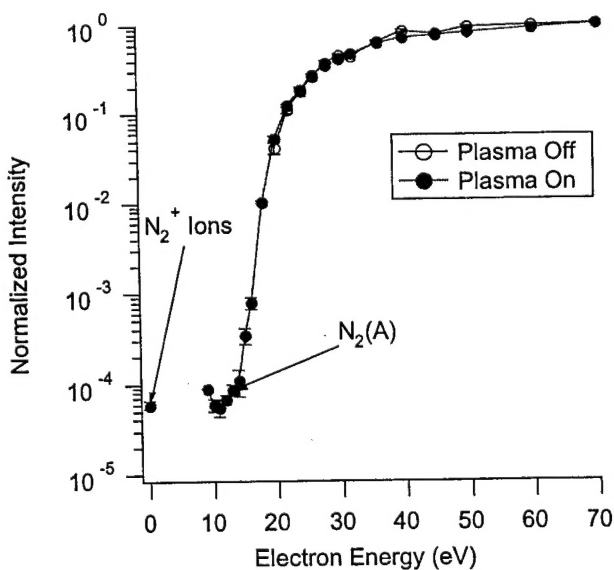ontains atoms, electronically excited molecules, and molecular ions. In his experiments, Pollard [22] used 38 MHz rf excitation and reported N_2 dissociation fractions as high as 60% for 2% N_2 seeded in He. Pollard inferred the production of He metastables, but he did not measure the number densities of N_2 metastables ($A\ ^3\Sigma_u^+$) or

molecular ions in the resultant supersonic beams. We have characterized an 13.56 MHz rf discharge supersonic jet source employing OES of the plasma plume and TOF-APMS of the species in the terminal supersonic beam. TOF-APMS data acquired using the apparatus in Fig. 2 allow us to quantify the fluxes and kinetic energies of atoms, ground-state and excited state molecules, and plasma-generated ions. The normalized intensity data shown in Figs. 5 and 6 demonstrate ground-state ^4S nitrogen atoms are the predominant reactive species in the terminal beam. The shift in the ionization threshold (appearance potential) of the 14 amu QMS

Fig. 6. TOF-APMS (28 amu) data characterizing an 13.56 MHz rf discharge N atom source.

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beam signal is direct evidence of the presence of N atoms. The contributions of N_2 metastables and N_2^+ ions to the terminal beam are very small by comparison (Fig. 6). Appropriate calibration of these signals will allow quantitative determination of the beam composition. Moreover, TOF analysis will allow the kinetic energies of N atoms, N_2 metastables, and N_2^+ ions to be determined. These calculations will be performed before the research is submitted for peer-review and archival publication.

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